

Influence of CO pretreatment on the activities of CuO/ γ -Al₂O₃ catalysts in CO + O₂ reaction

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Abstract

The influence of CO pretreatment on the properties of CuO/ γ -Al₂O₃ catalysts was investigated by X-ray diffraction (XRD), temperature programmed reduction (TPR), and infrared spectroscopy (IR). The activities of the treated catalysts were measured in low-temperature CO oxidation reaction (≤ 200 °C). It is shown that CO pretreatment at 250 °C mainly results in the reduction of crystalline CuO to Cu⁰ and dispersed Cu²⁺ to Cu⁺. CO–Cu⁺ interaction is much stronger than those of CO–Cu²⁺ and CO–Cu⁰, and as a result, CO molecules adsorbed on Cu⁺ are the main species on the fresh and CO pretreated catalysts exposed to CO stream at temperatures of 100 °C and higher.

For the low-temperature CO oxidation reaction, the activities of CuO/ γ -Al₂O₃ catalysts are intimately related to the operation temperature, copper oxide loading amount and CO pretreatment. CO conversions are promoted evidently with increasing operation temperatures. At the set operation temperatures, maximum CO conversions are always reached over the catalysts with a copper oxide loading amount of 0.6 mmol Cu²⁺/100 m² Al₂O₃, which is close to the dispersion capacity of copper oxide on γ -Al₂O₃, i.e., 0.75 mmol Cu²⁺/100 m² Al₂O₃. CO conversions over the catalysts following CO treatment are much higher than those over the fresh catalysts with the same amount of copper oxide. It is concluded that for low-temperature CO oxidation, dispersed copper oxide species are the primary active component, and the dispersed Cu⁺ species plays a significant role.

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1. Introduction

Copper-based catalysts have attracted much attention for their outstanding catalytic properties in environmental catalytic area during past decades [1–11]. Especially, CuO/ γ -Al₂O₃ catalysts have been widely used in a variety of catalytic reactions including CO oxidation, water–gas shift reaction, NO_x abatement, etc. [5–11]. This kind of catalysts is also regarded as one of the candidates that would replace existing economically unbenign precious-metal-containing catalysts in some heterogeneous catalytic processes [12–14]. A large number of studies have been conducted for understanding the properties of CuO/ γ -Al₂O₃ catalysts (in particular, the interaction between copper oxide and the support) and improving their performances in catalytic reactions [15–19].

As such, insightful information on this kind of catalysts has been obtained.

Nevertheless, due to the complexity of catalytic reaction, much more information still remains unclear. For instance, stable CO oxidation at lower temperature is a subject of significant relevance to fuel cell operation [20–22], but a consensus on the mechanism of this reaction over catalysts containing noble metals or copper has not been reached. Severino et al. found that CuO/ γ -Al₂O₃ catalyst with a copper oxide loading amount of 5 wt% is the most active in CO oxidation. They attributed this high activity to the contribution of dispersed copper oxide species on the surface of γ -Al₂O₃ [5,19,23]. This is supported by Laine's study, which proved that the formation of bulk Cu⁰ and CuAl₂O₄ spinel is the main reason that the activity of CO pre-reduced Cu/Al₂O₃ catalyst is decreased during CO oxidation [24]. In contrast, Park et al. [8] and Pierron et al. [25], on base of their independent studies, suggested that CO oxidation mainly proceeds on crystalline copper oxide. Moreover, Jernigan et al. investigated the

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influence of oxidation states of copper in CO + O₂ reaction, which suggested that metallic copper is the most active and with increasing copper oxidation states the activity decreased [26].

We have done a series of studies on CuO/ γ -Al₂O₃ catalysts previously, trying to understand the interactions between copper oxide and γ -Al₂O₃ support at atomic level by taking the surface structure of γ -Al₂O₃ into consideration [27–31]. The states of copper oxide species, and their contributions to catalytic reactions, e.g., NO + CO reaction, are reasonably described at different loading amounts [28,29,32]. Very recently, we found that CO pretreatment has a positive contribution to the performances of CuO/ γ -Al₂O₃ catalysts in CO oxidation [33]. In order to elucidate this effect, in this paper, the properties of CuO/ γ -Al₂O₃ catalysts following CO pretreatment and the activities of the treated catalysts in CO oxidation at various operation temperatures have been investigated in detail. It is concluded that surface dispersed copper oxide is the active component in this reaction, in particular at lower operation temperatures (≤ 200 °C), and Cu⁺ species induced by CO pretreatment (reduction) plays a significant role.

2. Experimental

2.1. Catalyst preparation

γ -Al₂O₃ was purchased from Fushun Petrochemical Institute in China, and was calcined at 700 °C for 7 h before being used for catalyst preparation. BET surface area is 155.9 m² g⁻¹. CuO/ γ -Al₂O₃ catalysts were prepared by wet impregnation of γ -Al₂O₃ with an aqueous solution containing a required amount of Cu(NO₃)₂. The samples were dried at 110 °C overnight, and then calcined at 500 °C in air for 5 h. For simplicity, the resultant catalysts are denoted as *x*Cu/Al, e.g., 0.3Cu/Al corresponds to the catalyst with a copper oxide loading amount of 0.3 mmol Cu²⁺/100 m² γ -Al₂O₃.

CO pretreatment for CuO/ γ -Al₂O₃ catalysts was conducted in a quartz tube. Before switched to CO, a CuO/ γ -Al₂O₃ catalyst was pretreated in a N₂ stream at 100 °C for 1 h. After cooling down to room temperature, the catalyst was exposed to a CO–N₂ stream (1.6% CO by volume, at atmospheric pressure) at a rate of 8.4 mL min⁻¹, and was heated to 10 °C min⁻¹ and held for 1 h at 250 °C. The treated catalyst was cooled to room temperature in a N₂ stream. The resultant catalysts are denoted as *x*Cu/Al–CO, e.g., 0.3Cu/Al–CO corresponds to the CuO/ γ -Al₂O₃ with copper oxide a loading amount of 0.3 mmol Cu²⁺/100 m² γ -Al₂O₃ following a CO pretreatment.

2.2. Instrument

XRD patterns were recorded on a Philips X'pert Pro diffractometer using Ni-filtered Cu K α radiation (0.15418 nm). The X-ray tube was operated at 40 kV and 40 mA.

In situ IR spectra of CO molecules adsorbed on CuO/ γ -Al₂O₃ catalysts were recorded on a Nicolet 5700 FT-IR spectrometer at a spectral resolution of 4.0 cm⁻¹. CO adsorption was performed

by exposing a self-supporting wafer of a catalyst (about 10 mg), mounted in a commercial controlled environment chamber (HTC-3), to a stream of CO–N₂ mixture (10% CO by volume) at a rate of 5 mL min⁻¹ for 30 min. IR spectra were recorded at 25 °C and various target temperatures. For the case of adsorption on CO-pretreated catalysts, catalysts pretreatment was done for the CuO/ γ -Al₂O₃ catalysts which have recorded the IR in the HTC-3 following the same procedure as that in the quartz tube.

TPR was carried out in a quartz U-tube reactor connected to a thermal conduction detector (TCD) with H₂–Ar mixture (7.3% H₂ by volume) as reductant. One hundred milligrams of sample was used for each measurement. Before switched to the H₂–Ar stream, the sample was pretreated in a N₂ stream at 100 °C for 1 h. TPR starts at room temperature at a rate of 10 °C min⁻¹.

The activities of the CuO/ γ -Al₂O₃ catalysts in CO + O₂ reaction were measured in a flow micro-reactor with a gas composition of 1.6% CO, 20.8% O₂ and 77.6% N₂ by volume at a space velocity of 30,000 mL g⁻¹ h⁻¹, 25 mg catalyst was used for each measurement. The catalysts were pretreated in a N₂ stream at 100 °C for 1 h before being switched to the reaction gas stream. Tail gas was analyzed using gas chromatograph with a TCD. Two columns for gas separation, the one packed with 13X molecular sieve (30–60 M) being for separating O₂, N₂ and CO, the other packed with Porapak Q being for separating CO₂.

3. Results and discussion

3.1. XRD results

Fig. 1 shows XRD patterns of various CuO/ γ -Al₂O₃ catalysts. For the fresh catalysts, no characteristic peaks associated with crystalline CuO are detected in the patterns of catalysts 0.3Cu/Al and 0.6Cu/Al. Several such peaks with significant intensities ($2\theta = 35.5^\circ, 38.7^\circ$) [PDF-ICDD (card no. 41-0254)] appear in the pattern of catalyst 1.2Cu/Al, as shown in the top pattern in panel A. As a result, combined with previous studies, which prove that the dispersion capacity of copper oxide on the surface of γ -Al₂O₃ is 0.75 mmol Cu²⁺/100 m² Al₂O₃ [27], it is reasonable to suggest that copper oxide species are highly dispersed on the surface of γ -Al₂O₃ when copper oxide loading amounts are ≤ 0.6 mmol Cu²⁺/100 m² Al₂O₃.

CO treatment leads to some evident changes in the XRD patterns of the resultant CuO/ γ -Al₂O₃ catalysts, intimately depending on copper oxide loading amount. For catalysts 0.3Cu/Al–CO and 0.6Cu/Al–CO, the XRD patterns are identical to those of fresh catalysts with the same copper oxide loading amount, i.e., no peaks associated with copper oxide species (or their reduced derivatives) are detected. Dramatic change is observed in the pattern of catalyst 1.2Cu/Al–CO. The characteristic peaks of crystalline CuO disappear completely, instead, several peaks associated with metallic Cu appear at ($2\theta = 43.2^\circ, 50.3^\circ$) [PDF-ICDD (card no. 4-0836)], indicating that CO treatment leads crystalline CuO to be reduced to Cu⁰. Nonetheless, it is worth noting in this stage, it is

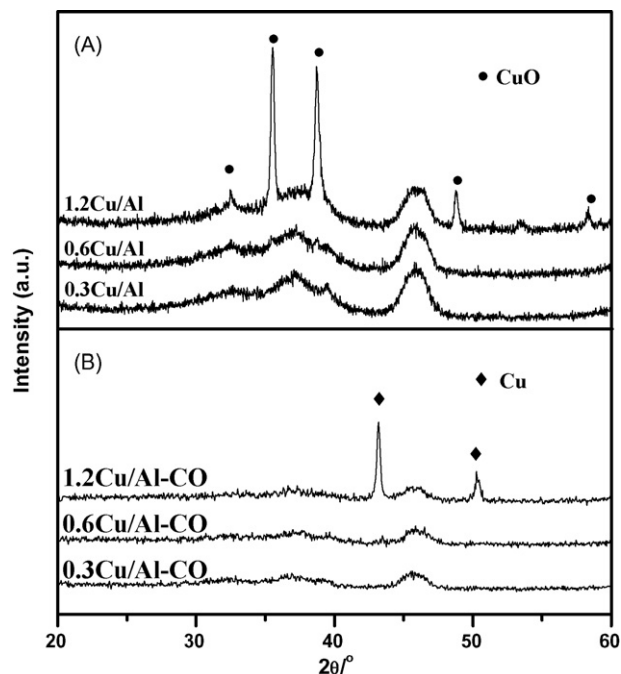


Fig. 1. XRD patterns of various CuO/ γ -Al₂O₃ catalysts: fresh (panel A) and CO-treated (panel B).

hard to tell exactly what changes surface dispersed copper oxide species underwent following CO treatment. So, TPR and in situ CO-IR were used to approach the state of dispersed copper oxide before and after CO treatment.

3.2. TPR results

TPR profiles of various CuO/ γ -Al₂O₃ catalysts are shown in Fig. 2. For the fresh catalysts, the profiles are changed evidently with increasing copper oxide loading amount. A peak with H₂ consumption maximum at \sim 247 °C appears in the profile of catalyst 0.3Cu/Al. In contrast, a much stronger peak with H₂ consumption maximum at \sim 207 °C is observed in the profile of catalyst 0.6Cu/Al. The profile of catalyst 1.2Cu/Al becomes complicated, two peaks appearing at \sim 217 and 240 °C. Combined with the above XRD results, the peaks appearing in the profiles of catalysts 0.3Cu/Al and 0.6Cu/Al can be assigned to the reduction of dispersed copper oxide species, the two peaks appearing in the profile of catalyst 1.2Cu/Al being to the reduction of dispersed copper oxide species (217 °C) and crystalline CuO (240 °C), respectively.

The H₂-TPR result shows that the central temperature of the low CuO loading sample (0.3Cu/Al) is higher than the high CuO loading sample (0.6Cu/Al). Some other research groups thought that is due to the formation of the copper aluminate species on the catalyst's surface [23,34]. However, the nature of the interaction between dispersed CuO and surface γ -Al₂O₃ is still not yet clearly understood. Based on the line of our previous studies [35–36], we tentatively discuss the possible interaction model between dispersed CuO and surface γ -Al₂O₃. As reported elsewhere, two kinds of surface vacant sites, e.g., octahedral and tetrahedral sites, were on the preferentially

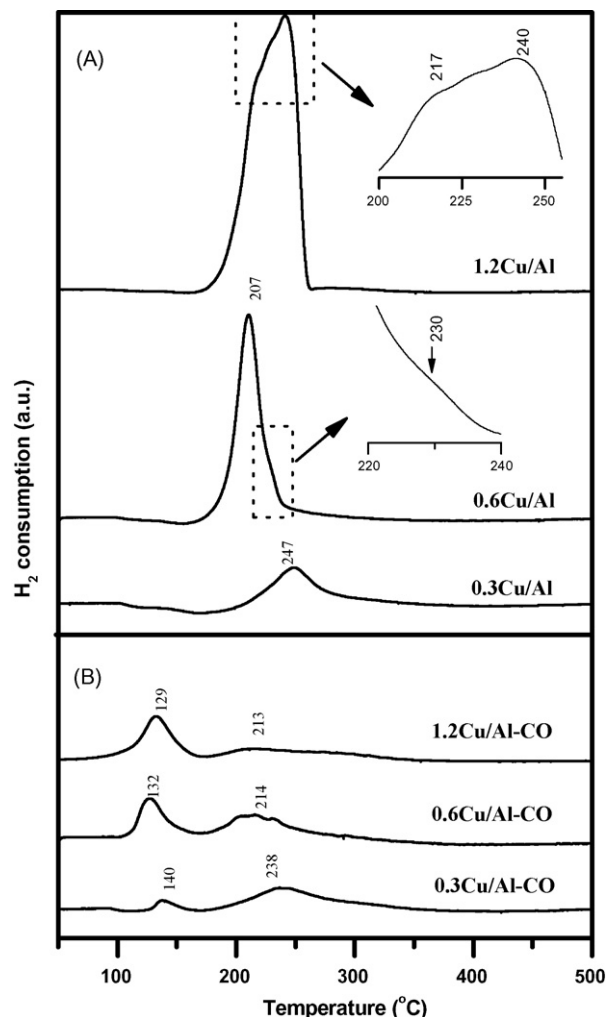


Fig. 2. TPR profiles of various CuO/ γ -Al₂O₃ catalysts: fresh (panel A) and CO-treated (panel B).

exposed (1 1 0) plane of γ -Al₂O₃ [36–37]. And γ -Al₂O₃ can be assumed to consist of particles formed by one-dimensional stacking of C- and D-layers. The exposure possibilities of these two layers are equal, as suggested by others [38]. Based on the consideration of the incorporation model proposed by Chen and Zhang [36], the surface structures of the dispersed copper oxide species could be proposed. In addition, the copper oxide would occupy the octahedral sites when the calcined temperature is below 750 °C [35,36]. Accordingly, the dispersed copper oxide species on the surface of the γ -Al₂O₃ support can be schematized, as shown in Fig. 3. For a CuO/ γ -Al₂O₃ sample, the dispersed copper oxide species could be tentatively described as the incorporation of a Cu²⁺ ion into the surface octahedral vacancy, and then one oxygen anion associated with the cation will stay at the top of the occupied site forming capping oxygen, for charge compensation, as shown in Fig. 4. From this model, it can be seen that Cu²⁺ is surrounded by six O²⁻ ions which dispersed in C-layer to form a surface octahedral copper oxide species. In contrast, for the dispersed copper oxide in D-layer, the Cu²⁺ is surrounded by five O²⁻ ions to form a defective octahedral copper oxide species. It is well established that the stability of the symmetric hexa-

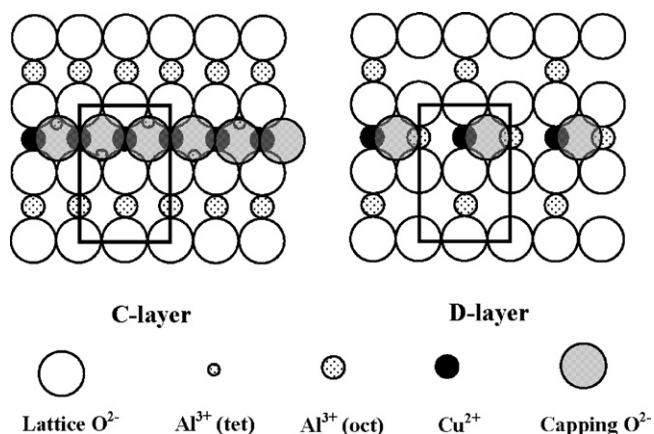


Fig. 3. Schematic diagram for the dispersed copper oxide species on the (1 1 0) plane of γ - Al_2O_3 .

coordinate is better than that of the asymmetric penta-coordinate. Therefore, the copper oxide species dispersed in D-layer's octahedral vacancy should be much more facilely reduced than the one dispersed in C-layer's octahedral vacancy.

As reported previously, the dispersion capacity of the CuO on the γ - Al_2O_3 support is $0.75 \text{ mmol Cu}^{2+}/100 \text{ m}^2 \gamma\text{-Al}_2\text{O}_3$ when the calcination temperature is lower than 750°C . For 0.3Cu/Al sample, the Cu^{2+} ions of the dispersed copper oxide would preferentially incorporate into C-layer's octahedral sites to form a stable structure, as discussed above. For 0.6Cu/Al sample, the Cu^{2+} ions of the dispersed copper oxide would incorporate into both C- and D-layer's octahedral sites. In this case, when TPR procedure was carried out, the dispersed Cu^{2+} ions are attacked by H_2 molecules, and the Cu^{2+} in the D-layer's octahedral sites would be reduced easily. Thus the reduction temperature of the 0.6Cu/Al is lower than that of the 0.3Cu/Al in H_2 -TPR results, e.g., 207°C corresponding to the reduction of the dispersed Cu^{2+} ions in D-layer and 247°C corresponding to the reduction of the dispersed Cu^{2+} ions in C-layer. In fact, a trace of a shoulder-peak ($\sim 230^\circ\text{C}$) (as shown in Fig. 2 for the brushfire profile) could be observed in 0.6Cu/Al sample, which means that the shoulder-peak ($\sim 230^\circ\text{C}$) corresponding to the reduction of the dispersed Cu^{2+} ions in C-layer. In addition a hydrogen spill over decreases the reduction temperature of the copper oxide dispersed in C-layer

in 0.6Cu/Al sample due to the prior reduction of the Cu^{2+} ions dispersed in D-layer. Namely, after the reduction of the dispersed copper oxide in D-layer the formed metallic copper species will dissociate and activate the hydrogen, which in turn will promote the reduction of the copper oxide dispersed in C-layer, resulting in the second reduction peak shifting to lower temperature and forming shoulder-peak [39]. This result is also supported by Larsson's study, which found that the reduction temperature of Cu3Al is higher than the Cu6Al, although both of them are from the reduction of the dispersed copper oxide species [23].

TPR profiles of these CuO/ γ - Al_2O_3 catalysts are changed greatly following CO treatment, and the most striking change is manifested by the appearance of a new peak at $129\text{--}140^\circ\text{C}$, as shown in panel B of Fig. 2. Moreover, some other features also become evident by comparing the three profiles: (1) the peak at $\sim 129\text{--}140^\circ\text{C}$ is very small in the profile of catalyst 0.3Cu/Al, but significantly intensifies in the profiles of catalysts 0.6Cu/Al and 1.2Cu/Al, in which the peak does not appear to be changed greatly with varying copper oxide loading amounts. This peak can be assigned to the reduction of Cu^+ species ($\text{Cu}^+ \rightarrow \text{Cu}^0$) arising from the partial reduction of surface dispersed Cu^{2+} species during the process of CO treatment; (2) the change in the peaks at temperature higher than 200°C is in the reverse trend, i.e., the peak intensity is diminished steadily with increasing copper oxide loading amounts. Combined with that for the peak at $129\text{--}140^\circ\text{C}$, this result conveys some interesting information: dispersed Cu^{2+} species that strongly interact with γ - Al_2O_3 support are hardly to be reduced by CO at 250°C (i.e., at a copper oxide loading amount of $0.3 \text{ mmol Cu}^{2+}/100 \text{ m}^2 \text{ Al}_2\text{O}_3$), the amount of such kind of species is reduced due to the effect of CuO dispersed into the D-layer's octahedral sites; most of crystalline CuO has been reduced to Cu^0 following CO treatment at 250°C .

3.3. IR results

To further explore the states of copper species in the CuO/ γ - Al_2O_3 catalysts before and after CO treatment, IR spectra of CO molecules adsorbed on these catalysts under various conditions were recorded, and are shown in Fig. 5. The spectra present several striking features:

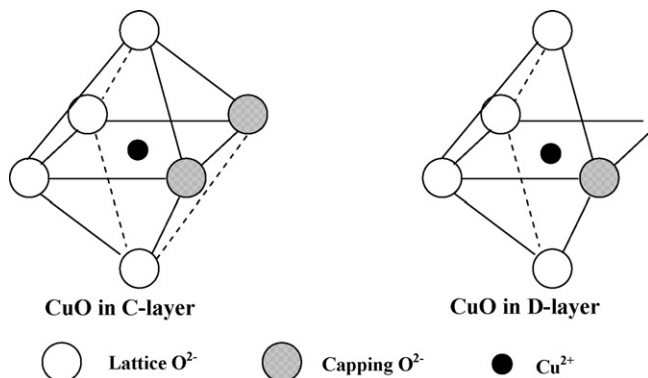


Fig. 4. Tentative model of the surface dispersed copper oxide species formed on the (1 1 0) plane of γ - Al_2O_3 .

- (1) All the spectra, fresh or CO pretreated, are predominated by a strong peak with vibrational frequency at $2090\text{--}2110 \text{ cm}^{-1}$ at the adsorption temperatures of 100°C and above.
- (2) For the catalysts following CO pretreatment, irrespective of the adsorption temperature, the spectra are predominated by a strong peak at $2090\text{--}2110 \text{ cm}^{-1}$. In contrast, this peak only gains a very weak intensity in the spectra of fresh catalysts at the adsorption temperatures below 100°C .
- (3) Besides this strong peak, another two peaks with relatively weaker intensities are also detectable at $2170\text{--}2180 \text{ cm}^{-1}$ and $\sim 2057 \text{ cm}^{-1}$ at the adsorption temperatures below 100°C , whereas resolution is worse than that at $2090\text{--}2110 \text{ cm}^{-1}$.

To date, a large number of studies have been done before, the IR spectra of adsorbed CO molecules on copper species (single crystals or copper oxide supported other metal oxides) are well defined. Roughly, the adsorption of CO molecules

on Cu^{2+} , Cu^+ , and Cu^0 gives rise to peaks with characteristic vibrational frequencies at about $2220\text{--}2150\text{ cm}^{-1}$, $2160\text{--}2080\text{ cm}^{-1}$, and below 2130 cm^{-1} , respectively, and of these the most stable is CO-Cu^+ [17,40–43]. Accordingly, it is

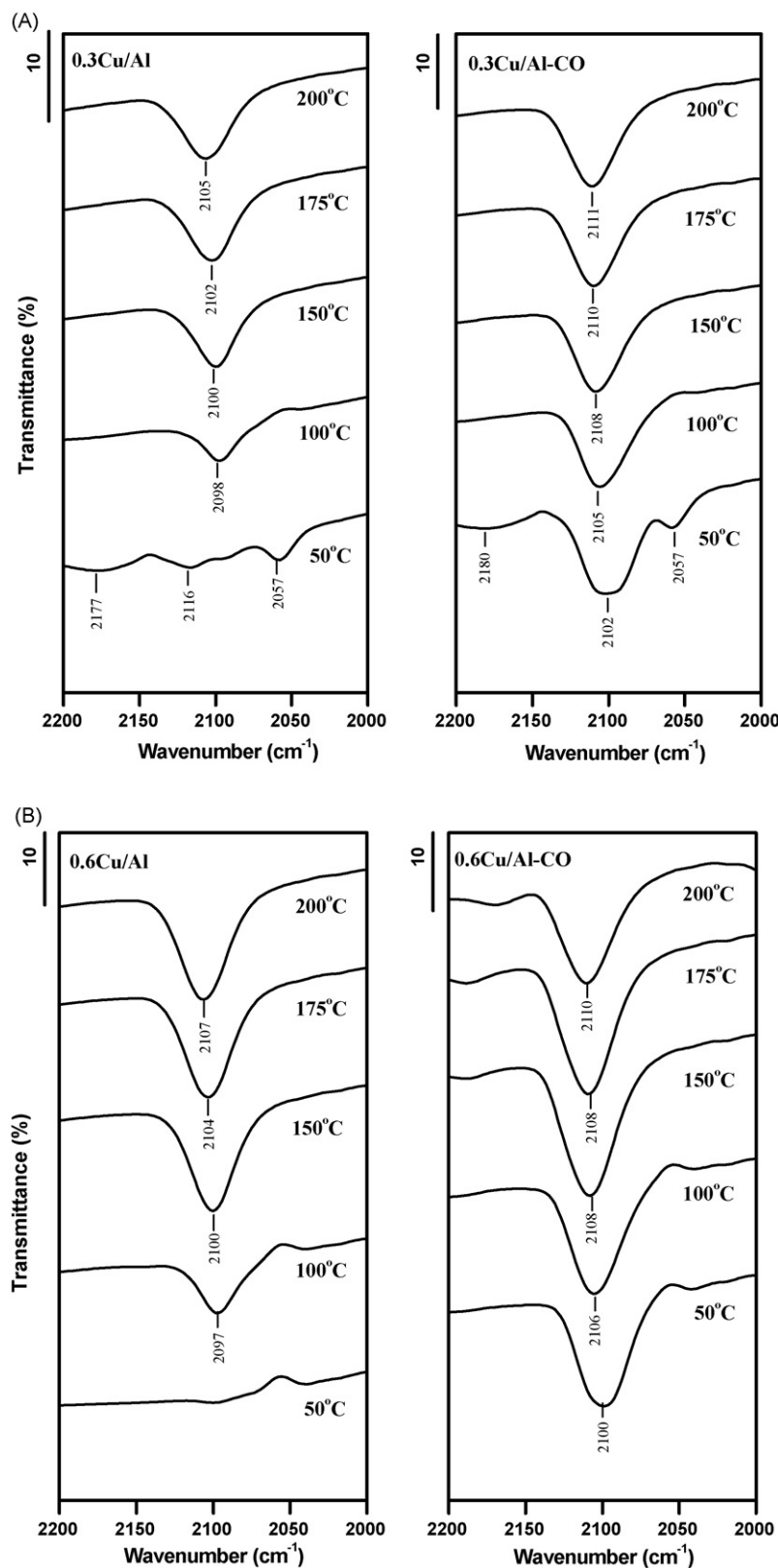


Fig. 5. IR spectra of CO adsorbed on various $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalysts. Adsorption temperatures are shown in the figure.

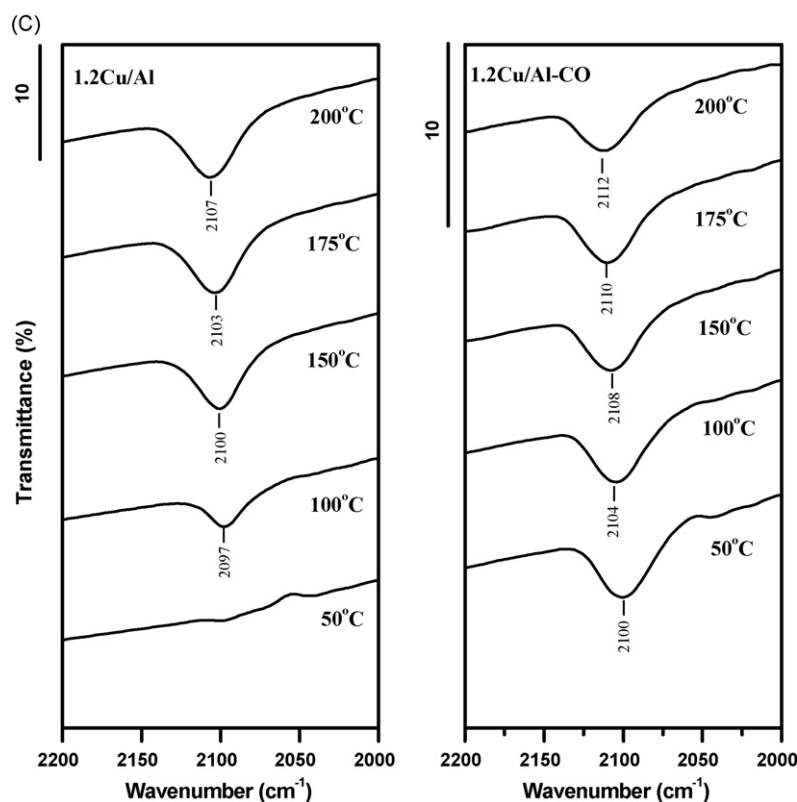


Fig. 5. (Continued).

reasonable to suggest that the predominant peak at 2090–2110 cm^{-1} in the present spectra is mainly corresponding to vibration of CO molecules adsorbed on Cu^+ , and such kind of adsorbing CO molecules is the most stable species on the $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalysts in the CO stream at temperatures $\leq 250^\circ\text{C}$. This is in good agreement with the above TPR results, which have shown that CO pretreatment at 250°C leads crystalline CuO to be reduced to Cu^0 and part of dispersed Cu^{2+} to Cu^+ .

3.4. Activities of $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalysts

Activities of various $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalysts (defined as CO conversion) were measured at different operation temperatures, and are shown in Fig. 6. It can be seen: (1) CO conversion are dramatically promoted with increasing the operation temperature, reaching 100% at 200°C over catalysts $0.6\text{Cu}/\text{Al-CO}$ and $1.2\text{Cu}/\text{Al-CO}$; (2) copper oxide loading amount also significantly influences the activities of the catalysts freshly prepared and CO pretreated. At the set operation temperatures in Fig. 6, CO conversions of copper oxide loading amounts at $0.6\text{ mmol Cu}^{2+}/100\text{ m}^2\text{ Al}_2\text{O}_3$ are much higher than those at $0.3\text{ mmol Cu}^{2+}/100\text{ m}^2\text{ Al}_2\text{O}_3$, but it is not obvious that CO conversions be improved greatly with increasing copper oxide loading amount from 0.6 to $1.2\text{ mmol Cu}^{2+}/100\text{ m}^2\text{ Al}_2\text{O}_3$; (3) at all the operation temperatures, CO conversions over the CO-pretreated catalysts are much higher than those over fresh catalysts, (4) whereas the initial states of copper oxide species in the catalysts are evidently different, i.e., only Cu^{2+} species are present in the fresh catalysts

and various copper species (Cu^{2+} , Cu^+ , Cu^0) combined with CO molecules in the treated catalysts, CO conversions reach maximum values in 10 min (first sampling) and remain stable at longer elapsed time, suggesting that this reaction does not require an induction process.

For reasonably linking the activities of $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalysts to a specific state of copper species, Fig. 7 in detail shows the influence of copper oxide loading amount on CO conversions over various catalysts. Interestingly, at an operation temperature of 175°C , CO conversions reach maximum values at a copper oxide loading amount of $0.6\text{ mmol Cu}^{2+}/100\text{ m}^2\text{ Al}_2\text{O}_3$ over fresh and CO-pretreated catalysts, decreasing slightly at $1.2\text{ mmol Cu}^{2+}/100\text{ m}^2\text{ Al}_2\text{O}_3$. At 200°C , CO conversions level off at copper oxide loading amounts of $0.6\text{ mmol Cu}^{2+}/100\text{ m}^2\text{ Al}_2\text{O}_3$ and higher over both kinds of catalysts. Combined with the above characterizations (XRD, TPR and IR), these results confirm that dispersed copper oxide species are the main active component for CO oxidation. Moreover, the states of these dispersed copper oxide species that are present in the reaction atmosphere, i.e., Cu^{2+} , Cu^+ or Cu^0 , can also be tracked. Both Figs. 6 and 7 clearly indicate that CO conversions over CO pretreated catalysts are much higher than those over fresh catalysts at the operation temperatures of 200°C and below, suggesting that CO pretreatment results in more active copper species for the reaction. On the other hand, TPR result has proved that a considerable amount of Cu^+ species is produced following CO pretreatment at 250°C , and as such; it is reasonable to conclude that the presence of Cu^+ species plays a significant

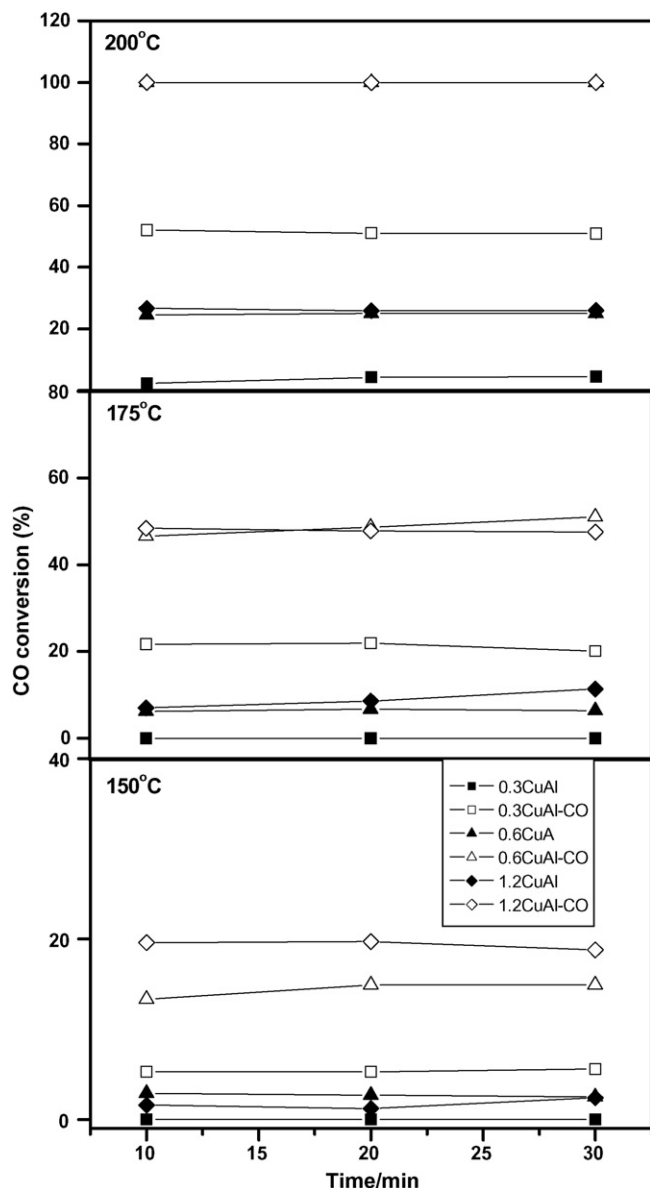


Fig. 6. Activities of CuO/ γ -Al₂O₃ catalysts at different operation temperatures.

role in low-temperature (≤ 200 °C) CO oxidation over CuO/ γ -Al₂O₃ catalysts.

For a completion, the influence of the elapsed time of CO pretreatment on the activity of CuO/ γ -Al₂O₃ catalysts was also investigated. CO conversions over the catalyst with a copper oxide loading amount of 0.6 mmol Cu²⁺/100 m² Al₂O₃ following a CO pretreatment of different elapsed time were measured at different operation temperatures and are shown in Fig. 8. It can be seen that, at the set operation temperatures in the figure, CO conversions initially increase with increasing the elapsed time of CO treatment, and reach maximum values at 30 min, and thereafter, remain constant. As a consequence, it can be concluded that CO pretreatment of 1 h has enabled all surface dispersed copper oxide species which can be reduced by CO at 250 °C to be available for the reaction to proceed.

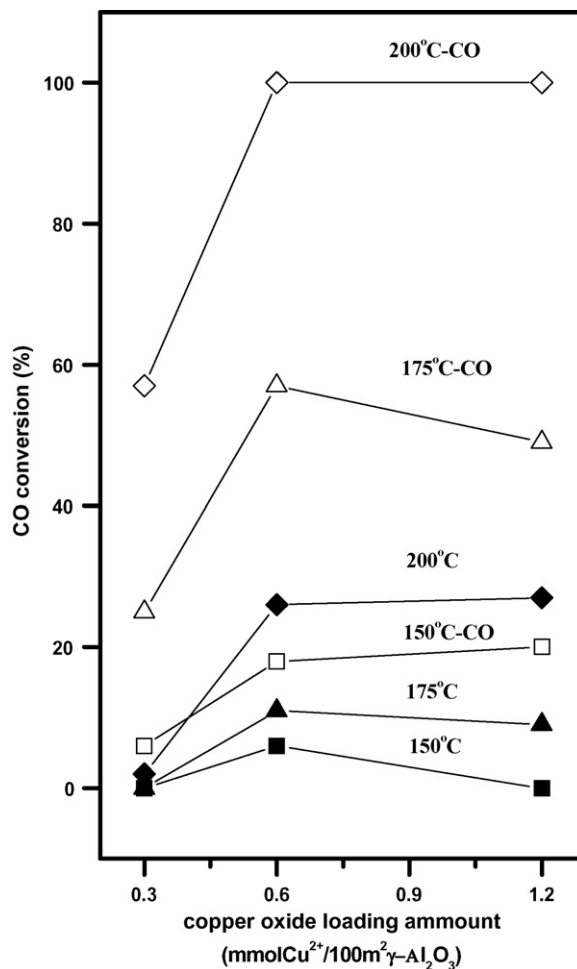


Fig. 7. Influence of copper oxide loading amount on the activities of CuO/ γ -Al₂O₃ catalysts at different operation temperatures.

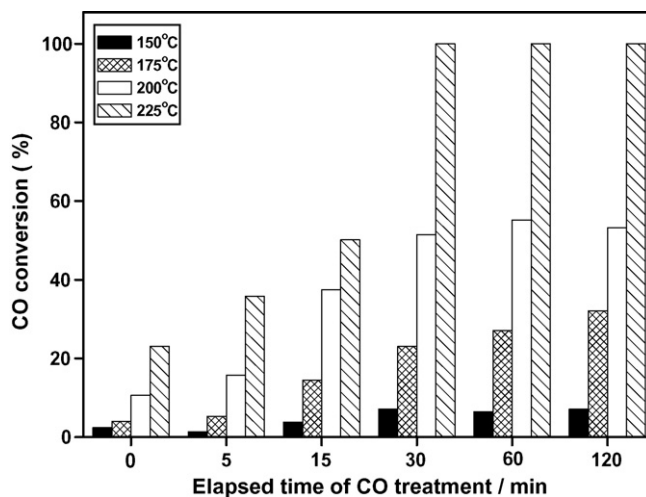


Fig. 8. Activity of CuO/ γ -Al₂O₃ catalyst with a copper oxide loading amount of 0.6 mmol Cu²⁺/100 m² Al₂O₃ following CO pretreatment of different elapsed time. The operation temperatures are shown in the figure.

4. Conclusion

The influence of CO pretreatment on the activities of CuO/ γ -Al₂O₃ catalysts in CO oxidation reaction was investigated. CO

pretreatment at 250 °C results in the reduction of crystalline CuO to Cu⁰ and dispersed Cu²⁺ species (partially) to Cu⁺. For the reaction proceeding at the operation temperatures of 200 °C and below, dispersed copper oxide species are the main active component, and CO pretreated catalysts are much more reactive than fresh catalysts. The CO pretreatment-induced promotion in the activities of the CuO/ γ -Al₂O₃ catalysts is attributed to the presence of dispersed Cu⁺ species, in other word, dispersed Cu⁺ species plays a significant role in low-temperature CO oxidation (≤ 200 °C).

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